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Thermal vacuum deposition of transparent conductive layers on semiconductor electrode tools for electrochemical machining of engineering products

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Abstract

This paper proposes a novel process for electrochemical engraving of metals without a need for stencils and photolithography. It dwells upon the features of receptions of electrodeposition films on a semiconductor tool electrode for electrochemical machining. The analytical equations to calculate the necessary thickness of a film are obtained. The technique of drawing films by thermal transpiration on vacuum plant VUP-4 is observed. The authors study a technology of making and designing the photo-active electrode tool, based on Cu/Si structure. The electrical and optical properties of a semiconductor thin plate have been investigated. The paper analyses the results of electrochemical machining by electrode tools with various thickness of an electrodeposition film. The theory and method of making, experimental results and an application of the semiconductor tool electrode are presented in this paper.

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Keywords: electrochemical machining; vacuum thermal deposition; semiconductor; transparent film; electrode tool; electrochemical marking

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1. Introduction

Electrochemical machining (ECM) is one of the non-traditional machining techniques; it can achieve a wanted shape of a surface using metal dissolution by electrochemical reaction and can be applied to metals such as hardened, high-strength and heat-resistant steel. ECM is necessary to advance a wide variety of industries, such as mechanical engineering, aerospace, automotive, electronic etc. [1-5].

Except forming surface finish also plays a vital role on the functional properties of the components such as wear resistance, energy loss due to friction etc. Engraving processes have been continuously developed due to high demand in various fields [6-7]. Manufacturing processes can be categorized according to the type of energy used in the process itself, such as mechanical, chemical, electrochemical, electrical and laser processes. The electrodischarge machining (EDM) machine converts the electrical energy into thermal energy in the plasma discharge channel during the spark discharge. The thermal energy melts and vaporizes workpiece material during the process [1,8]. The high temperature also generates the thermal stress in the workpiece. Laser surface treatment results in the homogenization and refinement of microstructures, change in the chemical composition, and phase transformation [9-10].

At the ECM there is no mechanical contact, thus no thermal nor mechanical stress is brought into the material. The hardness of the metal does not influence the material removal rate and the process shows almost no toolwear.

One of effective marking methods on conductive surfaces is electrochemical marking (ECMr) [11-12]. ECMr is also a good way to evaluate sheet metal formability. Knowing the level and distribution of strain in the critical areas of the stamping is the key with this technique. ECMr grid patterns are ideally suited for this purpose [13-14].

Typical installations of ECMr use solid electrode tools (ET) and a stencil with hollows in the image of the picture being marked, there being no electrolytic flow canal; the process is carried out by means of electrolytic damping of a porous layer. It limits the marking depth. Besides, such stencils allow to apply a limited number of markings, require special materials and printers or using photolithographic methods for printing.

The installations having the minimized and equal inter-electrode gap (IEG) size, along the whole surface and providing the conditions for the uniform electrolytic flow allow actualizing the ECM advantages to the full extant [15].

In a photoelectrochemical cell for ECMr one of electrodes is executed from a semiconductor material on which the light image is projected. Depending on voltage direction, a material of electrodes, a design of an electrochemical cell and a used electrolyte, the image can be formed owing to electroplated coating, anodic dissolution of an electrode or in electrolyte volume (photoelectrochromic effect) [1,4,16-19]. The conductivity of semiconductor is several order of magnitude is less, than at metals and electrolytes, therefore for planar optoelectronic devices it is necessary to provide conditions for equipotential a current lead on all square light absorption surfaces.. For this purpose on a semiconductor surface superimpose a thin film metals or electroconductive oxides of metals. At sampling of a spending pellucid covering for contact to a semi-conductor material it is necessary to consider optical and electric parametres of this film, and also property of contact a film – the semiconductor [18-21].

The ultimate goal of the present research activities was to develop new technological processes leading to highly effective optical coatings of a semiconductor wafer for application in electrochemical engraving and marking.

2. The theoretical analysis

It is obvious that increasing the thickness of the deposited film, on the one hand, reduces the surface electric resistance of the film, but, on the other hand, leads to reduced transparency of the film. In [22] for definition of a necessary thickness of a film suggest to use the integrated factor of criterion *Q*, defined as the ratio of the normalized average transmittance to normalized resistivity. However, such optimisation, in our opinion, is justified for solar cells, light-emitting diodes, liquid crystal meshes of displays etc., where it is necessary to achieve integrated efficiency of photoelectric transformation of all element. In case of ET for ECMr, first of all, it is necessary to be aimed to equipotential surfaces, because the optical transmittance even if will decrease, all the same will be homogeneous for all surface. The decrease in transparency of the coating to actinic radiation, which accounts for the maximum of spectral photosensitivity of the semiconductor, can be compensated by increasing the light intensity. Besides, at correct sampling of a thickness of a covering it is possible to reduce light losses at reflexion from a semiconductor surface. The coefficient of reflexion *A* is defined by Fresnel's formula:

$$A = \left(\frac{n-1}{n+1} \right)^2, \qquad (1)$$

where n is the refractive index.

For silicon over the range visible light a mean n = 3.9, calculation by formula (1) shows, that light losses on reflexion attain 35 %. If the waves reflected from an external and internal surface of a thin film are in phase opposition as a result of an interference these two waves are mutually relaxed. The greatest easing will occur at equality of amplitudes of these waves which occurs under a condition $n_0 = \sqrt{n}$, where n_0 - refractive index of a film.

Optical dispersion in semiconductors does not allow to solve a problem of elimination of reflexion completely. When choosing the thickness of the antireflection film on the premise, to reduce the reflection waves, which have maximum spectral photosensitivity. For tin dioxide, which is often used in optoelectronic devices [18,19,22], no in red light is approximately equal to 2, therefore, when the coating thickness d satisfying the condition $n_o d = \lambda/4$ can achieve significant attenuation of reflection. The corresponding calculation for wave-length λ = 0.9 μm gives a value of d = 0.1 μm. Thus, the SnO_2 coating thickness must be a multiple of the size of 0.1 μm.

For metal films, the situation is more complicated because of strong absorption of light. For damped waves, the intensity of the transmitted light P at the depth d is determined according to Bouguer's law

$$P = P_0 \exp\left(-\frac{4\pi}{\lambda} n\chi\, d \right), \qquad (2)$$

where P_0 is the intensity of the incident wave; χ is the absorption coefficient.

For example, at $n\chi$ = 1 in metal on ways, numerically equal to wave length, intensity of an incident wave decreases approximately in 10^5 times. For copper n = 0.62, and magnitude $n\chi$ = 2.57, for aluminium n = 1.44 and $n\chi$= 5.23. Let's define a depth of penetration in a copper film for wave length λ = 0.9 μm. Calculation by formula (2) gives value $d \approx 0.028$ μm. Therefore, transparent metal films for optoelectronic devices have a thickness of about 10 nm, and can perform the antireflective function. Moreover, as metal films are characterised by a considerable coefficient of reflexion of light, it is necessary to cover them with a clarifying dielectric film in addition. This clarifying antireflection coating simultaneously performs a protective anti-corrosion function.

Let's define dependence of electric parametres of a thin film on its thickness. For semi-conductor planar ET there is the specific lapse of machining connected with an anode drop in a film of a conductor at removal from a current lead. It is thus broken equipotentiality surfaces that leads to emersion of a density gradient of a current in places of equal light exposure. We will size up this lapse.

Let's observe a semi-conductor plate in the thickness d with surface radius r_1 on which the thin film by thickness h is put (Fig. 1).

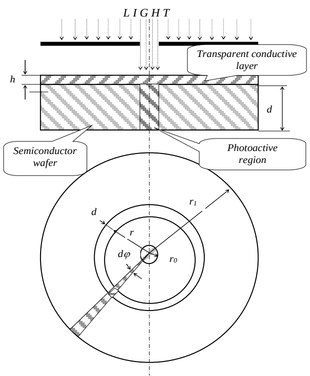


Fig. 1. Estimate drawing for determining the voltage drop in the conductive transparent film.

The current lead is carried out on film ambit not shown). On a plate the light stain with radius r_o is projected. From symmetry reasons it is obvious, that the maximum anode drop will be in case the light sonde gets to the plate centre.

For definition of resistance of a film we will gate out the part of sector restricted to an angle $d\varphi$ and rounds with radiuses r and $r+dr$. Resistance of this section of sector will be equal

$$dR(d\varphi, dr) = \frac{\rho dr}{rhd\varphi}, \tag{3}$$

where ρ is the resistivity of a film.

The resistance of all sector restricted $d\varphi$ is given by

$$dR(d\varphi) = \int_{r_0}^{r_1} \frac{\rho dr}{rhd\varphi} = \frac{\rho}{hd\varphi} \ln \frac{r_1}{r_0}. \tag{4}$$

Since the sector is connected "in parallel", the total resistance of the film on the site of the current supply to the light spot will receive

$$\frac{1}{R} = \int_0^{2\pi} \frac{hd\varphi}{\rho \ln \frac{r_1}{r_0}} = \frac{2\pi h}{\rho \ln \frac{r_1}{r_0}},$$

from here follows

$$R = \frac{\rho \ln \frac{r_1}{r_0}}{2\pi h}. \tag{5}$$

The general resistance of a thin film and the lighted section of the semiconductor is given by

$$R_\Sigma = \frac{\rho \ln \frac{r_1}{r_0}}{2\pi h} + \frac{\rho_{ph} d}{\pi r_0^2}, \tag{6}$$

where ρ_{ph} is the resistivity of the semiconductor at illumination (the light resistivity).

Drop of potential in a semi-conductor electrode ΔU is given by

$$\Delta U = j\pi r_0^2 R_\Sigma = j\left(\frac{\rho r_0^2 \ln \frac{r_1}{r_0}}{2h} + \rho_{ph} d\right). \tag{7}$$

From here follows, that the maximum drop of potential ΔU will be under a condition

$$r_0 = \frac{r_1}{\exp 0.5} \approx 0.607 r_1 , \tag{8}$$

at this size the light spot will be the maximum error processing caused by the voltage gradient on the film surface. The relative value of this error e is defined by the expression

$$\varepsilon = 0.092 \frac{\rho r_1^2}{\rho_{ph} h d_1} , \tag{9}$$

and this should be considered when determining the thickness of the coating.

From the equation (2) follows, that ρ_{ph} depends on depth d. For practical estimated calculations it is necessary to define experimentally magnitude ρ_{ph} for the chosen magnitude of light exposure. With rather good accuracy it is equal

$$\rho_{ph} = \rho_0 \frac{I_d}{I_{ph}} ,$$

where ρ_0 is the specific dark resistance of the semiconductor; I_d / I_{ph} is the relation of a dark current to a photocurrent at used voltage (i.e. in the field of photocurrent saturation).

Let's define a thickness of a copper film for magnitude ε=0.1. Typical parametres of semi-conductor plates in our experiments were the following: r_1 = 30 mm; d = 0.38 mm; I_d / I_{ph} =180. Matching calculation by equation (3) gives value h = 10 nm.

Thus, with the account of estimated character of the spent calculations, it is possible to assume, that for reception of satisfactory results ECM the thickness of a metal film should not exceed 10 … 20 nm.

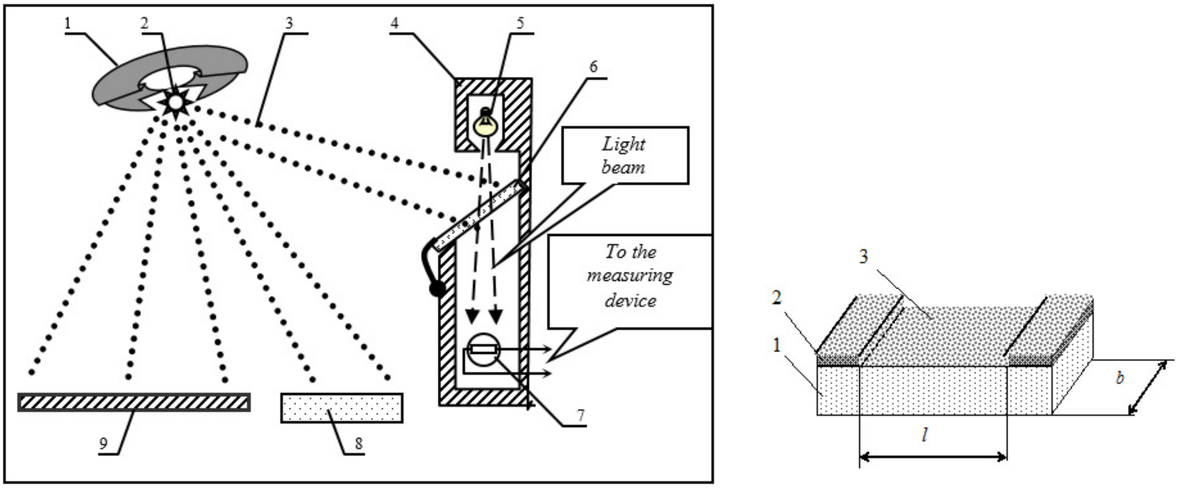
3. Experimental technique

For film deposition we used a method of thermal spraying of metal in a vacuum installation VUP-4, which allows you to adjust the thickness of the sprayed layer with the indicator deposition, located on the remote control. The locations of the sensor indicator thickness in a vacuum chamber and its main elements is shown in Fig. 2. (a). Measurement method based on the proportional relationship between the film thickness control of the glass 6 and its coefficient of optical transmittance. The measuring circuit of the indicator are collected in a bridge circuit, one arm of which includes the photoresistor SF-1 (on the basis of cadmium sulfide). Before you start deposition a variable resistor of the bridge circuit established the necessary thickness. A measuring device included in the emitter circuit of the matching load balanced DC amplifier, which is the second diagonal of the bridge. In the coating process, the light flux through the check glass decreases, the resistance of the photoresistor increases, the bridge unbalance, and when the deflection of the measuring device by an amount proportional to the thickness of the deposition layer, the unlocking circuit of the evaporator and the process is terminated.

Calibration of the indicator deposition was carried out separately for each of the sprayed substance, the type of evaporator and the corresponding geometry of the deposition. In conditions of isotropic evaporation analytical calculation of the film thickness h was performed according to the formula

$$h = \frac{\Delta m \sin \Theta}{\gamma 4 \pi R^2} , \tag{10}$$

where Δm is the total weight of evaporated substance; Θ is the angle of incidence of a stream of evaporating corpuscles on a surface; γ is the substance density; R is the distance from the evaporator to a surface.



(a) (b)

Fig. 2. (a) Location scheme of the indicator gauge thickness, semiconductor wafer, and "witness" in a vacuum chamber: 1 – heater; 2 – evaporable substance; 3 – the flow of evaporated particles; 4 – the capsule of the measuring sensor; 5 – light source; 6 – glass plate; 7 – photoresistor; 8 - "witness"; 9 - semiconductor wafer; (b) "Witness" for electrooptical measurements: 1 – a glass plate; 2 – the bonding pad; 3 – an deposition film.

It should be noted that the thickness of the deposition layer on the glass plate 6 (Fig. 2. (a)) is not equal to the thickness of the deposition layer on the semiconductor substrate 7. These thicknesses are proportional, and the proportionality factor depends on the geometry of irradiation, namely, the distance from respective surfaces to the evaporated material and the angles of inclination of the respective surfaces to the flow of evaporated particles. Even more complex relationship between optical transmission ratios of the respective layers.

With this in mind, for a more accurate measurement of optical transmittance and surface resistance of films on a semiconductor wafer in the coating process, next to it put "the witness" 8 (check glass substrate, Fig. 2. (b)). "Witness" (Fig. 2. (b)) consisted of a glass plate 1 positioned on contact pads 2. The width of the contact strips b equal to the distance between the contacts l. In this case, the resistance between contact pads R_p representation for equal specific surface resistance (or resistance per square). In this case, the resistance R_p of deposited thin film 3 depends on the film thickness:

$$R_p = \frac{\rho\, l}{bh} = \frac{\rho}{h},$$

where ρ is the resistivity of a film.

In general the resistivity is not equal to normal (reference) specific resistance of the material and depends on the conditions of film formation, therefore, the error in thickness measured by this method is small and is more than 10% [10]. The presence of a "witness" in our experiments allowed to determine the coefficient of optical transmittance of the film and its surface resistance. For a more accurate determination of the thickness of the deposited film laboratory balances LLDP-100g with a scale division of 0.05 mg were determined mass of the substance Δm deposition on a wafer. Film thickness h was determined by the equation $h=\Delta m/S\gamma$, where S is the square of a surface of a plate.

This formula can be used in case the dimensions of the evaporation surface is much less than the distance from the heater to the surface. In our experiments, the radius r of the plate (excluding the site for current lead a width of 0.5 cm) was 3.3 cm, the distance R to the evaporator 30 cm (Fig. 2. (b)). Relative non-uniformity ε of the thickness of the deposited film in the center and on the edges of the plate, defined by the equation (4) is equal to

$$\varepsilon = 1 - \frac{R^3}{(R^2 + r^2)^{\frac{3}{2}}}.$$

Calculation by this formula gives the relative non-uniformity of the film thickness is less than 2%, and this error is less than the error due to the voltage gradient on the surface of a semiconductor (10%, equation (3)).

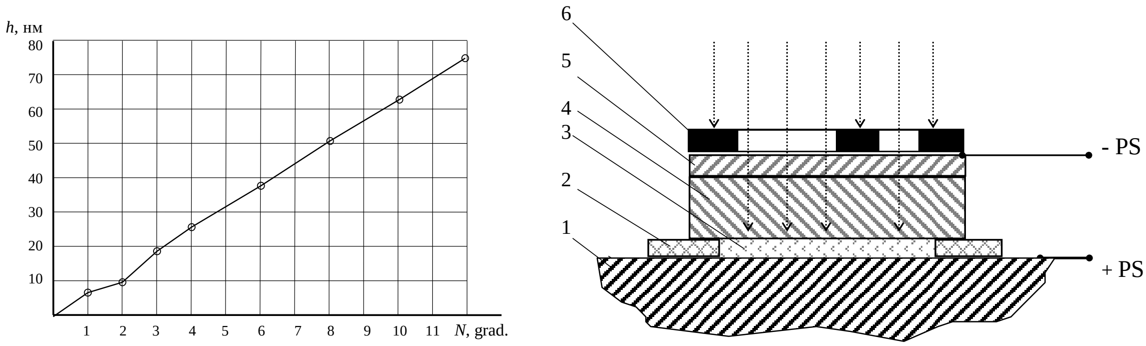
The table presents calculated values of the film thickness by measuring the mass of copper precipitated on a silicon wafer with a diameter of 76 mm. In our calculations we used the density value of "solid" copper $\gamma = 8{,}93 \cdot 10^3$ kg/m^3.

Table 1. Calculation of film thickness h measured mass Δm of copper precipitated on a silicon wafer with a diameter of 76 mm.

Δm, mg	0.25	0.40	0.75	1.05	1.55	2.55	3.05
h, nm	6	10	19	26	38	63	75

Graph to determine the thickness of the deposited film h on the testimony of indicating instrument N for this experiment is shown in Fig. 3. (a). Similar curves were constructed for each of the deposition substance separately. For deposition used the analytical grade metals from Al, Cu, Ag, Ni, Cr, and conductive oxides SnO_2, CdO.

Scheme of electrochemical cell for the study of technological capabilities of ET on the basis of monocrystalline silicon with various conductive coatings are presented in Fig. 3. (b).



(a) (b)

Fig. 3. (a) Graph to determine the thickness of the deposited film h on the testimony of N indicating instrument; (b) Scheme of the electrochemical cell to study a silicon ET: 1 – workpiece; 2 – dielectric strip; 3 –IEG filled with electrolyte; 4 – semiconductor wafer; 5 – transparent conductive layer; 6 – photostencil; the arrows indicate the direction of the light flux; PS – power source

For definition of technical characteristics of ECMr through the photomask 6 image projected on the transparent conductive layer 5 connected to the negative terminal IE. The positive terminal of the PS was connected to the workpiece 1. Through the gap formed by dielectric spacers 2, the electrolyte was passed. The current distribution on the working surface 3 of the semiconductor is determined by the illumination of the relevant parts of its outside surface. The required operating voltage between the electrodes was determined on the basis of current-voltage characteristics from the condition of saturation of the photocurrent.

4. The conclusion

Studies have shown that for electrochemical machining with semi-conductive transparent electrode tools for metal-coating for copper films better the results, you have the ET processing of single crystal cream nievoy plate thickness of 0.38 mm and a diameter of 76 mm (p -type KDB-10). On the surface of this wafer in a vacuum chamber VUP-4 was coated film thickness of 15 nm. The chamber pressure was 10^{-4} Pa, during evaporation plate was heated to 500°C. The transmittance of a copper film in the optical range was 45-55 % and surface electrical resistance was 2.1 Ω.

The present electrode tools is expected to be useful in various applications such as micro-texturing of surface, electrochemical marking, fabrication of microgrooves in an hydrodynamic bearing, etc.

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